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Research paper

Thermodynamic optimisation of the biofuel production based on mutualism

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ABSTRACT

Recently, we have introduced a new bioeconomic indicator in order to avoid the difficulties in evaluating the process and technologies for sustainability. In this paper, we wish to improve this new indicator for the analysis of sustainability. Indeed, the indicator has been based on the exergy analysis of dissipation and irreversibility, and it was proven in some social and technical application. In this work, a more general definition has been introduced in order to use it in any evaluation of sustainability. In particular, it has been applied to improve the biofuel production obtained by microorganisms, starting from the biophysical behaviour of the microorganisms themselves. Indeed, in industrialised countries, the management of CO₂ emissions represents one of the present compelling issues. In this context, the improvement of the energy efficiency, and its rational use, can be considered a fundamental economic strategy for the sustainable development of the industrialised countries. Our indicator takes into account all these requests for the development and sustainability, resulting a very interesting thermoeconomic quantity to be used by decision makers. Moreover, it is used to prove that mutualism can represent a new approach for the optimisation of biofuels production.

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1. Introduction

During all the history of humanity, the impact of technology and engineering on society is being an evidence, from the metallurgy era to the industrial revolution, from the steam engine to electronics and information technologies. The link between technology and engineering represents the basis for any change in society (Clay and Fong, 2013).

Often, not all the results related to the scientific and engineering researches are directly introduced in application fields, because the use these results is a decision-making process for technical problems, and often, it is brought only by an economic or financial approach.

Business activities play a fundamental role in the control of every stage of the value creation and production chain, and, consequently, of their impacts on the use of resources and on the natural environment (Corbett, 2009). On the other hand, just business activities can constitute a powerful tool to achieve sustainability (Tang and Yeoh, 2007).

Indeed, today, sustainability and sustainable development represent a fundamental topic of investigation with particular regards to their link to global warming and local pollution (Corbett,

2009). There are several issues and questions related to sustainability and sustainable development which have to be solved or improved. For instance, a first problem associated to sustainability is how to measure the resources (Sciubba and Zullo, 2011, 2012), which implies the construction of an effective method to quantify the resources themselves. A second problem can be identified in the empirical evidence that most natural species display a multitude of modes of interaction, from indifference to competition, from antagonism to adaptation, etc. Moreover, a third problem is represented by the ability of the natural species to the substitutable use of their resources (Sciubba and Zullo, 2012).

For example, as regards the use of resources, recently operations management has been introduced also in relation to circular economy and sustainability (de Sousa Jabboura et al., 2019). Operations management is an engineering approach to:

- The management of the physical resources required for production, whether the product be a manufactured item or a service (Constable and New, 1976);
- The design, operation, and improvement of the systems in order to obtain the primary products and services (Chase et al., 2006);

The efficient management of these resources and systems is fundamental in relation to the great number of people employed.

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The sustainable development has been introduced even in the natural and environmental sciences with the aim of attracting the interest of political and business stakeholders in order to meet the needs of the present generations without compromising the ability of the future ones to meet their own needs (WCED, 1987).

Sustainability is by its nature a multidisciplinary topic. In the last decades, researches on sustainability have continuously been growing in number with a wide variety of interest. Of course, we have to focus our attention on the fundamental topics of sustainable development: Environment, Economy and Society (Giddings et al., 2002; Tracey and Anne, 2008).

These subjects of study must be linked with the technological improvement, which represents the boost of development in: clean technologies, labour changes and management, and new markets.

In this context, some considerations must be introduced. During the decades of the XX century, economical choices have always become more a product of social and political requirements than the results of a scientific approach. Moreover, recently the roles and responsibilities of individuals have been redefined and the decision making has become decentralised (Ruth, 2006). The technological innovations of the production systems revolutions have been driven by economic growth and changes on society (Polaskya et al., 2019). The improvements in the knowledge in physical, engineering and health sciences, have played a fundamental role in the economists approaches to the complexity of the present society.

At the end of the XIX century, mathematical approaches to economic activity were developed, based on natural-law-like principles (Ackerman, 2002), obtaining objective functions for households and firms and also conditions of equilibrium for decisions in the economy. On the other hand, when conditions for optimality have not been achieved, policy of interventions was introduced in order to establish just the foreseen economic equilibrium. To do so, the main instruments used have been: changes in relative prices of goods and services, introduction of taxes, or changes in the forms of markets themselves.

But, the approach based on equilibrium and stability has been contrasted (Ackerman, 2002), also by the thermodynamic approach to open systems, based on steady state conditions. So, economy, as living systems, develops within the constraints related to finite resources of the Earth system. This new approach attracted the economists interest to the ecological problems, allowing the inclusion of the resources and wastes in the economical theories.

Economy, finance, production, transportations, etc., all constitute human activities. But, the man is part of the ecosystem, consequently, all his activities must be considered in relation to the laws of nature. What can link all these (apparently) different topics one another? Energy is the quantity essential for all these activities (Stern, 2017); indeed, from production to services, from economy to finance, etc. energy is required. But, energy is a thermodynamics topic of research, so we must develop an approach able to link economy to thermodynamics.

In particular, this approach can be useful for all complex and multidisciplinary themes, including biofuels, due to their wide diversity of topics and details to be considered. Indeed, in relation to biofuels there are several aspects that must be taken into account such as:

- Ethics: biofuels must be produced without any reduction of the cultures for human supply;
- Technics: biofuels must be produced by using technical approaches without generating a relevant increase in local pollution;
- Economics: biofuels must be able to generate labour.

Two main risks on actual society have been identified by Rittmann (2008) about fossil fuel consumption and their relative depletion:

- The possibility of geopolitical turmoil due to the scarcity of resources;
- The increasing amount of greenhouse gasses in the atmosphere.

Biofuels have been introduced in order to find an alternative way to fossil fuels, due to the depletion of the latter and to their related environmental issues (Nigam and Singh, 2011). So, some of required characteristics of the biofuels can be summarised as (Lang et al., 2001):

- Easy availability;
- Technical and environmental feasibility;
- Economic competitiveness.

One of the advantages of being generated from different biomasses is represented by diversification in terms of supply: each Country could produce locally the raw materials needed to biofuels production (Lee and Lavoie, 2013). Moreover, those which are derived from biomasses that perform photosynthesis during their living cycle, use CO₂ as a feedstock. Biofuels have been classified at least in three different generations, depending on the biomass feedstock from which they are originated as follows:

- The first generation biofuels, which are those derived from food yields (Immethun et al., 2016);
- The second generation biofuels, which are those derived from non edible biomasses, or lignocellulosic biomasses (Saladini et al., 2016), including the ones discarded from food and agricultural industry and urban wastes (Battista et al., 2016; Bensaid et al., 2012);
- The third generation biofuels, which are those derived from photosynthetic microorganisms as microalgae (Alaswad et al., 2015).

So, the main concerns related to the first generation of biofuels are the use of agricultural yields and all its consequences (including the competition with edible crops, the loss of biodiversity, land-use changes and water depletion Correa et al., 2019) which cannot be considered sustainable (Chowdhury and Loganathan, 2019) and ethical, while, for the second generation, it exists a barrier due to their energy and costs requirements (Carriquiry et al., 2011). Consequently, a development of new generation of biofuels (the third one) is required. Biofuels produced from microalgae and photosynthetic microorganisms are widely studied: they present many advantages such as:

- The non competition with edible crops;
- The absorption of CO₂ during their life cycle (Chisti, 2007; Mata et al., 2010);
- The relatively high efficiency in performing photosynthesis (Pols and Spahn, 2014).

Moreover, compared to the higher plants,

- Microalgae have major oil yield (delivering the highest quantity of lipids juxtaposed to all other biomass feedstock Ziolkowska and Simon, 2014);
- They need less water than terrestrial plants;
- They can grow in any kind of water (also in wastewater Leong et al., 2019) or non-arable land without competing with terrestrial crops;
- Their cultivation does not require pesticides or herbicides;
- A large variety of biofuels can be obtained from their biomass (Rodolfi et al., 2009).

On the contrary, their production process in large scale has not been yet largely developed (Rodolfi et al., 2009). The main drawbacks that make them not yet competitive with the fossil fuels have been noticed in costs of production and extraction compared to the amount of fuel obtainable per litre of culture (Enamala et al., 2018).

In this context, biofuel production must be analysed just to optimise their production process (Musa et al., 2019) due to the necessary transition from fossil fuels to renewable ones. Moreover, this requirement is also imposed by the legislation. Indeed, in the last decade biofuels have been developed also in order to fulfil government policies (Saravanan et al., 2018; Su et al., 2015). For example, as regards the European Union, the *Directive on the Promotion of the Use of Biofuels or Other Renewable Fuels for Transport* (2003/30/EC), the *Renewable Energy Directive* (2009/29/EC) which has been recently modified by the *Renewable Energy Directive II* (2018/2011/EC) in which the overall target for renewable energy sources use (to achieve within 2030) has been raised to 32%. In particular, for the sub-sectors of road and rail transport the minimum level has been set to 14%, with a limitation for biofuels of first generation due to their nature and to their Indirect Land Use Change (Commission, 2018).

So, in order to improve biodiesel production from living microorganisms, the idea of symbiotic cultures has been suggested in literature (Santos and Reis, 2014; Shurin et al., 2013; Kazamia et al., 2014; Cooper and Smith, 2015; Heimann, 2016) and, in this paper the use of our indicator will point out the improvement of the sustainability in the biofuels production. Indeed, the lipid production can be enhanced if the two symbionts take an advantage from the metabolism of the other one symbiont. Moreover, it could be a possible solution to create advanced biorefineries (Cho et al., 2015) by using a natural association's characteristic existing between the metabolisms of the species employed, obtaining a higher quantity of the desired raw materials (lipid production for the biodiesel case), jointly with less organic wastes (Ramanan et al., 2016) from the production processes.

The aim of this paper is just to propose new indicators useful to evaluate the processes, the services, etc., in summary the human activities in relation to their impact on the human life, on the environment and on the social economy introducing the econophysical and thermoeconomic approaches to optimisation, in order to reduce the environmental impact and to improve the human wellness. To use the introduced indicator, we will focus on the biofuels production by microorganisms, developing the biophysical optimisation of the lipid formation for biodiesel production and responding to the previous highlighted questions. In order to develop our analysis, we will introduce the definition of our indicator, but also its generalisation. Then, we will use the indicator in the analysis of two different cases, just studied by using other thermoeconomic approach, in order to verify its effectiveness. Lastly, we will use the indicator in the study of the biofuel production by microorganism, suggesting the mutualism as an optimisation method for the lipid production.

2. Methods

The aim of this paper is to link the economical and social approach to the thermophysical one, allowing the decision makers to improve their assessments for a really sustainable society and sustainable productive processes. In particular, we apply this approach to the biofuels production.

To do so, we must consider the fundamental quantities which are used in the different scientific areas of research:

- The Energy Intensity EI , defined as (Cleveland et al., 1984; Csereklyei et al., 2016; Agovino et al., 2019):

$$EI = \frac{E_{in}}{GDP} \quad (1)$$

where E_{in} is the energy used to obtain the value of GDP , and the GDP is the Gross Domestic Product which has classically been interpreted as the wealth of a country or of a productive system (Vincent and Hartwick, 1997; Hoekstra, 2019). Here, we suggest to consider the energy that can really be used in the process (the exergy), so a new definition can be introduced:

$$ExI = \frac{Ex_{in}}{GDP} \quad (2)$$

where Ex_{in} is the input exergy;

- The Labour Productivity, LP , defined as (OECD, 2019; Blain, 1996; Zhang and Dornfeld, 2007):

$$LP = \frac{GDP}{n_{wh}} \quad (3)$$

where $n_{wh} = n_w \cdot n_h$ is the total number of worked hours needed to obtain the GDP , with n_h number of worked hours and n_w number of workers;

- The Second Law Inefficiency η_λ , defined as (Lucia and Grisolia, 2019a):

$$\eta_\lambda = \frac{W_\lambda}{Ex_{in}} \quad (4)$$

where W_λ is the work lost due to irreversibility and friction (Bejan and Lorente, 2004):

$$W_\lambda = Ex_{in} - Ex_{out} - W \quad (5)$$

while Ex is the exergy and the subscripts in and out mean respectively inflow and outflow, while W is the work which can be expressed by the exergy balance (Bejan, 2006):

$$W = \sum_{\alpha} J_{ex,\alpha} + \sum_{\beta} Ex_{Q,\beta} - \Delta B - T_0 S_g \quad (6)$$

where:

- $J_{ex,\alpha} = \int_0^\tau \dot{m}_\alpha (e_\alpha - T_0 s_\alpha) dt$ is the flow exergy due to the α th mass flow;
- $Ex_{Q,\beta} = Q_\beta (1 - T_0/T_\beta)$ is the exergy transfer due to the β th heat transfer;
- $\Delta B = E + p_0 V - T_0 S$ is the accumulation of non-flow exergy;
- S_g is the entropy variation due to irreversibility, named entropy generation (Lucia, 2007, 2013b; Bejan, 2000; Sciaciovelli et al., 2015; Bejan, 1982, 1995; Bejan et al., 1996; Bejan and Lorente, 2004, 2010);

and the subscript 0 means environment, while \dot{m} is the mass flow, e is the specific energy, s is the specific entropy, Q is the heat exchanged, E is the total energy, S is entropy, T is the temperature, p is the pressure and V is the volume.

Now, considering that any process, interaction, cycle, etc. occurs in a definite time τ , the lifetime of this phenomenon then, for any process or interaction of any open system, and by following the Gouy–Stodola theorem (Bejan, 2006), the work lost due to irreversibility and friction W_λ , is proportional to the entropy variation due to irreversibility, as

follows:

$$W_{\lambda} = T_0 S_g = \sum_i \left(1 - \frac{T_0}{T_i} \right) Q_i - W - \Delta E + T_0 \Delta S + \sum_j \int_0^{\tau} dt \dot{m}_i (h_j + e_{k,j} + e_{p,j} + e_{ch,j} - T_0 s) + \sum_{\ell} \int_0^{\tau} dt \dot{n}_{\ell} (g_{\ell}^{\oplus} - ex_{ch,\ell}^{\oplus}) \quad (7)$$

where h is the specific enthalpy, and the subscripts k , p and ch mean kinetic, potential and chemical respectively, i and j are related to the number of fluxes of heat and mass respectively, \dot{n} is the molar flux, ν is the stoichiometric coefficient, g is the molar specific Gibbs potential, $ex_{ch} = y(\mu - \mu_0)_{T_0, p_0}$ is the molar specific chemical exergy at the reference atmosphere conditions, y is the molar fraction, μ is the chemical potential, \oplus means standard conditions and ΔS is the system entropy variation.

The energy variation ΔE during the life time τ results:

$$\Delta E = \sum_i Q_i - W + \sum_j \int_0^{\tau} \dot{m}_j (h_j + e_{k,j} + e_{p,j} + e_{ch,j}) dt \quad (8)$$

As a consequence of the previous equations related to the First and the Second Laws of Thermodynamics for open systems, it is possible to highlight that any change in the energy of the system can be expressed in terms of the transfer of:

1. Flows of matter across the system boundary, which bring internal, kinetic, chemical and other forms of energy;
2. Heat across the system boundary;
3. Performance of work developed by or on the system.

Consequently, an analogy between physics (or thermal engineering) and the interactions analysis among technical, economical and social effects, can be carried out. In bioeconomy, the thermodynamic quantities have been introduced in order to describe the socio-economic system as a biosystem. In engineering thermodynamics, the global effect of the different efficiencies, due to the different phenomena which occur in a thermal system, is considered by introducing only one overall efficiency that is the result of the multiplication of each single efficiency referred to each single effect (Grimaldi and Millo, 2015). Moreover, in physics the interaction is usually expressed by multiplying the physical quantities which describe the natural phenomenon.

Therefore, we consider the interaction between technical, economical and social effects by introducing a new indicator, synthesis of the previous ones, defined as:

$$I = \eta_{\lambda} \cdot ExI \cdot LP = \frac{W_{\lambda}}{n_{wh}} = \frac{T_0 S_g}{n_{wh}} \quad (9)$$

Generalising this relation we can state that the new indicator can be obtained as:

$$I = \frac{\text{exergy lost}}{\text{quantity related to the required effect}} \quad (10)$$

Now, we wish to introduce our results to some applications.

2.1. Thermodynamic cycles for solar power plant

The first application regards the use of our indicator in relation to the engineering analysis developed in Ref. Reyes-Belmonte et al. (2017). In this work, five thermodynamic cycles are coupled to a solar tower central receiver in order to compare their efficiencies also in relation to the operating working fluid. Indeed, the high temperature at the solar receiver is considered the key

Table 1

Net electrical power of the different cycles \dot{W}_{el} and relative calculated indicator I as defined in (11).

Cycle	\dot{W}_{el} [MW]	I
Standard Rankine	9.1	5.26
Standard Brayton	6.8	7.38
Brayton 750 °C	7.6	6.50
Brayton 1000 °C	9.4	5.06
Combined cycle	21.5	1.65
Brayton He	7.4	6.70
Brayton sCO ₂	10.4	4.48

quantity for selecting the optimal power cycle to match with the solar concentrator. The different cycles compared one another are: the subcritical steam Rankine–Hirn cycle, the open regenerative Brayton air cycle, configured at medium (750 °C) and high temperature (1000 °C), the combined cycle, the closed regenerative Brayton helium scheme and closed recompression supercritical carbon dioxide Brayton cycle (Reyes-Belmonte et al., 2017). Power cycles and working conditions are compared in relation to a reference thermal power supply by the receiver of 57 MW_{th}. Moreover, the environmental conditions are the same, with consequence to realise five different cycles, working at the same operational conditions.

As a consequence of these operational conditions, we can highlight that our indicator allows us to compare the cycles in relation to their sustainability.

So, for this application, we can define our indicator (10) as follows:

$$I = \frac{T_0 \dot{S}_g}{\dot{W}_{el}} \quad (11)$$

where T_0 is the environmental temperature, \dot{S}_g is the entropy generation rate and \dot{W}_{el} is the electric power. In order to numerically evaluate the indicator we use the data collected in the Ref. Reyes-Belmonte et al. (2017). Our results are summarised in Table 1. We can highlight that the indicator decreases when the electric power produced increases. So, the indicator assumes the lower value when the cycle is more efficient, which means that lower is the indicator, higher is the sustainable level of the cycle and our results are in agreement with the ones of Ref. Reyes-Belmonte et al. (2017).

2.2. Power cycle with a gas turbine with an absorption chiller

Now, in order to validate the indicator, we can consider a second example of use. We take under analysis a gas turbine cycle with an absorption chiller in two different configurations, as performed in Ref. Ahmadi et al. (2012):

- Gas turbine with inlet cooler;
- Gas turbine with inlet cooler and injection.

The use of this kind of plants is useful where the environmental temperature is high, in particular when the climate is arid or tropical. In this cases the intake air of the compressor is cooled in order to avoid the negative effect of high temperatures which limit the air mass intake, reducing the turbine useful output. The inlet air on the compressor is cooled by using an absorption chiller for increasing the gas turbine capacity (Mohanty and Jr., 1995).

A schematic diagram of the plant considered (and deeply analysed) in Ref. Ahmadi et al. (2012) is represented in Fig. 1, where the main plant elements are the compressor, the combustion chamber, the gas turbine, the heat recovery steam generator, the absorption chiller unit and the inlet cooler. As presented in

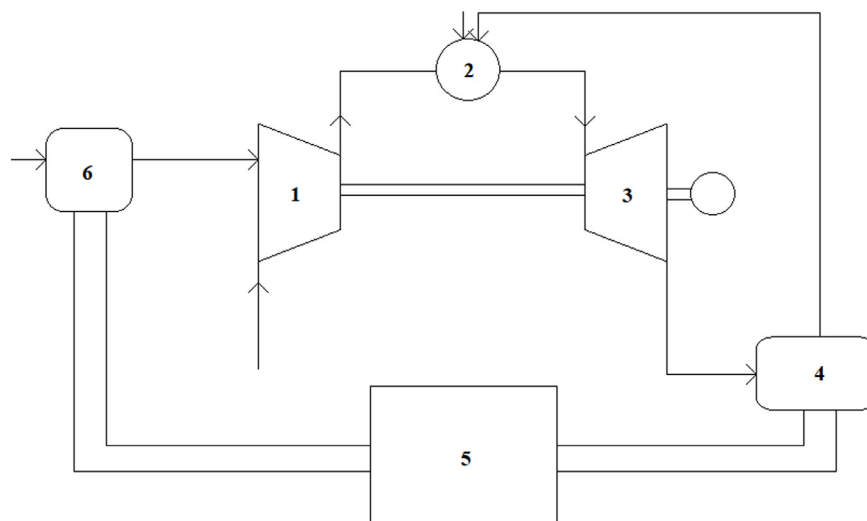


Fig. 1. The plant considered is composed by: a Compressor (1), a Combustion chamber (2), a Gas turbine (3), a Heat recovery steam generator (4), an Absorption chiller system (5), and an Inlet cooler (6).

Table 2

Power loss due to irreversibility $T_0 \dot{S}_g$ [MW] for each plant element, useful net power \dot{W}_n [MW] and the relative value of the indicator I , calculated as defined in (12) for two different configurations: A - Gas turbine with inlet cooler & B - Gas turbine with inlet cooler and injection (as presented in Ref. Ahmadi et al., 2012).

	A	B
Element	$T_0 \dot{S}_g$ [MW]	
(1) Compressor	6	6
(2) Combustion chamber	96	103
(3) Gas turbine	7	9
(4) Heat recovery steam generator	45	11
(5) Absorption chiller unit	5	5
(6) Inlet cooler	1	1
Net power output	\dot{W}_n [MW]	
	57	74
Indicator	I [-]	
	2.8	1.8

Ref. Ahmadi et al. (2012), the plants are compared considering the same reference environment and the same exergy inlet per unit of time $\dot{E}x_{in}$ which numerically corresponds to $\dot{E}x_{in} = 195$ MW.

In order to use our indicator, we define the it (10) For this application, as follows:

$$I = \frac{T_0 \dot{S}_g}{\dot{W}_n} \quad (12)$$

where T_0 is the environmental temperature, \dot{S}_g is the entropy generation rate and \dot{W}_n is the net power achieved in the cycle. The numerical results are summarised in Table 2, and they are obtained by using the data collected in Ref. Ahmadi et al. (2012). We can highlight that the indicator decreases when the efficiency of the cycle increases, in agreement with the results of the Ref. Ahmadi et al. (2012).

2.3. Biofuels production & mutualism

In our times, the growing attention to the reduction of the emissions of greenhouse gases is moving the strong dependence upon fossil fuels as sources of energy towards alternatives. Indeed, for example the land-based transport is gradually coming to abandon liquid hydrocarbons and internal combustion engines

for electrical power, even if, at present, for aviation transport and shipping, there are no viable alternatives yet. Consequently, this new sensibility towards the reduction of CO₂ emissions drives our energy production systems towards the development of liquid biofuels. Although the production of biodiesel and bioethanol has increased rapidly since the 1970s, at 30 – 40% per annum, the total energy production of bioethanol and biodiesel is only of the order of 10⁶ TJ in relation to the total global energy use of the order of 10⁸ TJ (Williams and Laurens, 2010).

So, we wish to introduce our results in the analysis of the third generation biofuels production. To do so, we must develop some considerations on biosystems.

To live, organisms have to interact with their environment, exchanging with it flows of matter and energy; thus, from a thermodynamic point of view involves the possibility to study them as open systems by using the First and the Second Law of Thermodynamics (Demirel and Sandler, 2002; Demirel, 2010; Lucia, 2015). Life could not exist without any interaction with the environment, so that it can be considered as the key factor of life, including the possible interactions with the other species present in the environment itself.

When more species co-exist in the same ambient, a natural phenomenon, called symbiosis, can occur. The term symbiosis was first introduced in 1879 by Heinrich Anton de Bary, referred to the living together of different interacting species of organisms (Oulhen et al., 2016). Symbiosis has represented, and still represents a fundamental component in Earth's life development and for the evolution of living organisms, as Stanley has pointed out (Stanley, 2006). So, symbiosis can be defined as the association between at least two distinct species of living organisms (Paracer and Ahmadjian, 2000). This association can persist on time for an undefined duration or for a finite time and can change its effects along the same period, depending also on the environment conditions in which the interaction takes place (Bronstein, 1994).

The interaction between living organisms can lead to an advantage for at least one of the symbionts or to a disadvantage or to nothing at all, and this different kinds of symbiosis that can occur in nature have been categorised, distinguishing the effects of the association between the organisms considered (Willey et al., 2013):

- Mutualism, which implies an obligatory interaction with a reciprocal benefit for both species;

- Cooperation, which implies a non-obligatory interaction with a reciprocal benefit for both species;
- Commensalism, which implies a positive relationship between the species, where one of them takes an advantage and the other is neutral to the interaction (usually the waste of one organism is used by the other one as a nutrient);
- Predation, which is a negative form of symbiosis, one organism is attacked and preyed by the other one;
- Parasitism, which is a complex interaction in which an organism (parasite) gains a benefit and the other one is damaged (host);
- Amensalism, which is an unidirectional interaction and implies the production by one organism of a compound that has a negative effect on the other one;
- Competition, which overcomes when both species need the same resource (nutrient) to live, the organisms can co-exist at lower levels or one organism can overwhelm the other one.

All these subcategories are useful from a theoretical biology standpoint to define and to classify all kind of interactions. However, over time it has emerged that from an experimental point of view, it is very difficult to distinguish in which category of symbiosis each single case analysed falls under (Willey et al., 2013), because they can switch from one form to another one during organisms life (Douglas, 1994), too. Moreover, there is not a universally recognised definition of all types of symbiosis and mutualism declinations (Martin and Schwab, 2013; Peacock, 2011; Boucher et al., 1982; Dimijian, 2000; Mazancourt et al., 2005; Munzi et al., 2019). So, following Paracer and Ahmadian (Paracer and Ahmadian, 2000) we adopt the term mutualism as the association in which each symbiont gets a benefit. However, in literature (Begon et al., 2006; Dodds and Whiles, 2020b; Glavič and Lukman, 2007; Dodds and Whiles, 2020a) other definitions have been introduced in relation to the cooperative interaction between species/organisms; some examples are the following:

- Detritivory, which is considered as a kind of commensalism, where one species gets a benefit from the other one that is no more alive (thus, the latter is neutral) (Begon et al., 2006);
- Facilitation, which is defined as any unidirectional benefit for one of the involved organisms (Dodds and Whiles, 2020b);
- Protocooperation, where both organisms get conditional benefits even if they are able to continue to live independently one from another (Glavič and Lukman, 2007);
- Synergism, which is considered the general non obligatory relationship in which the two organisms get benefit one from another (Dodds and Whiles, 2020a);
- Syntrophy, which is considered as a kind of mutualism and synergism where the metabolisms of the two species are complementary one to another (Dodds and Whiles, 2020a);

We suggest to consider that a complete review of the terminology associated to symbiosis is presented and discussed in Reference (Martin and Schwab, 2013).

Mathematical approach to mutualism is based on the predator/prey or consumer/resource interactions (Berryman, 1992). In this approach, the terms “type I” and “type II” functional responses are introduced in relation to the linear and saturating relationships respectively, between benefit provided to an individual of species 1 on the density of species 2.

The Type I functional response can be developed by introducing the Lotka–Volterra approach, obtaining that the change

in population density of the two mutualists results (Berryman, 1992):

$$\begin{cases} \frac{dN_1}{dt} = r_1 N_1 - r_{11} N_1^2 + r_{12} N_1 N_2 \\ \frac{dN_2}{dt} = r_2 N_2 - r_{21} N_2^2 + r_{22} N_1 N_2 \end{cases} \quad (13)$$

where N is the numerical density of the population of the two species (1 and 2), r_i is the intrinsic growth rate of the population, r_{ii} is the negative effect of within-species crowding and r_{ij} is the beneficial effect of a mutualistic partners density. Mutualism represents a logistic growth equation together with a mutualistic interaction. The latter results as the growth in population density of i -species due to the hereness of greater numbers of j -species, and the other way around. It includes also a saturation mechanism in order to avoid that the species densities increase indefinitely.

In 1989, the Lotka–Volterra equations were modified by Wright, who added a new term just to represent the mutualistic relationship. Moreover, in 1959, Holling improved the analytical analysis by introducing two constraints, as follows (Wright, 1989):

- There exists a relation of proportionality between the number of food items caught and the allotted searching time;
- There exists a second variable of time, which is distinguished from the search time: the handling time.

So, Holling obtained an equation for the Type II mutualistic functional response as follows (Wright, 1989):

$$\frac{dN_1}{dt} = N_1 \cdot \left[r_1 (1 - cN_1) + \frac{\beta N_2}{X + N_2} \right] \quad (14)$$

where $X = 1/(a\tau_H)$, τ_H is the handling time, a is the instantaneous discovery rate, c is the coefficient that takes into account the negative aspects of growth due to the interactions between species, $\beta = b/\tau_H$, b is the coefficient converting encounters with N_2 to new units of N_1 , and N_1 and N_2 are the densities of the two mutualists.

But, when we consider the two species of microorganisms (i.e. bacteria, bacteria/alga, alga/alga) living together, we consider that they absorb exergy Ex_{in} in different forms (heat, metabolites, etc.) and they release biofuels, bioplastics or other useful bio-products. The entropy generation will be obtained by evaluation of the photosynthetic contribution of each species and of the contribution of the interaction between the two species. This last contribution is the more difficult to be evaluated. So, we can directly obtain the evaluation of the efficiency of the symbiosis by considering the useful effect required, that in our case is the lipid mass production. Indeed, to produce biodiesel from photosynthetic microorganisms the fundamental parameters are the biomass productivity and the amount of lipids stored inside their cells. So, we consider that if the two species live separately they release the mass of products m_1 and m_2 respectively, which holds $m_1 h_f$ and $m_2 h_f$ respectively in terms of energy releases, where h_f is the formation enthalpy of the product which is the same in both cases. If the species live together, we aspect that they release $(m_1 + m_2)h_f$, while in the case of mutualism they release $(m_1 + m_2 + \Delta m)h_f$.

In this case the indicator (10) can be written as:

$$I = \frac{T_0 S_g}{Ex_{in}} = \frac{Ex_{in} - m h_f}{Ex_{in}} \quad (15)$$

where T_0 [K] is the environmental temperature, Ex_{in} is the inflow exergy [J], m is the lipid mass produced [kg], and h_f is the specific enthalpy of formation [J kg⁻¹]. Consequently, the indicator for the two processes results:

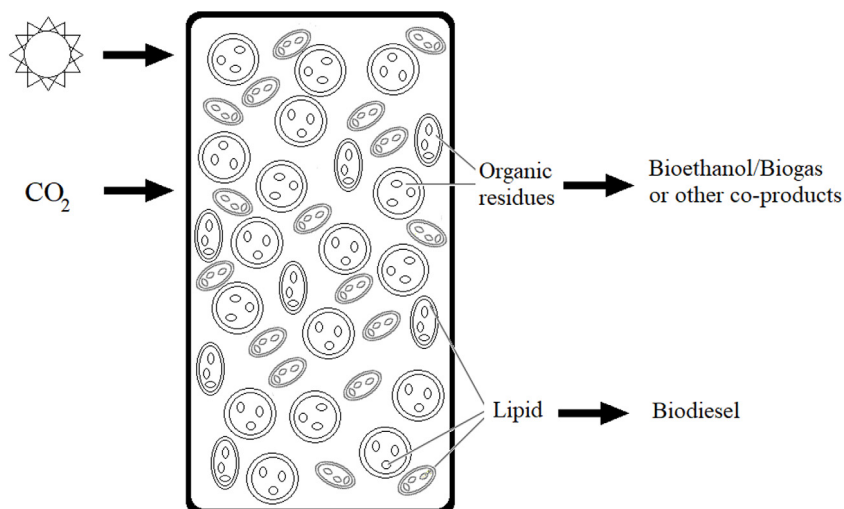


Fig. 2. Co-culture of two different micro-organisms performing symbiosis. Their biomass contains lipids, from which it is possible to obtain biodiesel. From the residual biomass other valuable co-products could be obtained. The symbiotic interaction leads to an exchange of metabolites, nutrients and other key factors for the growth of the microorganisms.

- non-mutualistic process:

$$I = \frac{Ex_{in} - (m_1 + m_2) h_f}{Ex_{in}} \quad (16)$$

- mutualistic process:

$$I_m = \frac{Ex_{in} - (m_1 + m_2 + \Delta m) h_f}{Ex_{in}} \quad (17)$$

We consider the process as a thermodynamic regenerative process and we can obtain that:

$$I_m = I + (I - 1) \cdot \frac{\Delta m}{m_1 + m_2} < I \quad \text{always} \quad (18)$$

which means that the mutualistic process is more sustainable because the related indicator is lower than the non-mutualistic process one.

Here we consider two different examples of co-cultivation. In each case, two different photosynthetic microorganisms were cultivated together in order to investigate their behaviour and their lipid and biomass productivity to produce biodiesel (and eventually other useful co-products from their biomass residues Saravanan et al., 2018, left after the process of lipid extraction, as shown in Fig. 2).

By using the data collected in Refs. Rashid et al. (2019) and Zhao et al. (2014), two different examples of comparison for the mutualistic and non-mutualistic cultivation can be summarised as follows:

- Coproduction of *Ettlia* sp. and *Chlorella* sp. (Rashid et al., 2019):

- *Ettlia* sp. lipid mass produced in mono-cultivation $m_1 = 30.3 \pm 4.7 \text{ mg L}^{-1}$;
- *Chlorella* sp. lipid mass produced in mono-cultivation $m_2 = 201.7 \pm 8.2 \text{ mg L}^{-1}$;
- Mutualistic lipid production of *Ettlia* sp. & *Chlorella* sp. $m_1 + m_2 + \Delta m = 353.7 \pm 6.0 \text{ mg L}^{-1}$;

- Coproduction of *Chlorella* sp. and *Monoraphidium* sp. (Zhao et al., 2014):

- *Chlorella* sp. lipid mass produced in mono-cultivation $m_1 = 370.6 \pm 177.3 \text{ mg L}^{-1}$;
- *Monoraphidium* sp. lipid mass produced in mono-cultivation $m_2 = 95.6 \pm 26.7 \text{ mg L}^{-1}$;

- Mutualistic lipid production of *Chlorella* sp and *Monoraphidium* sp. $m_1 + m_2 + \Delta m = 592.6 \pm 184.6 \text{ mg L}^{-1}$.

Using these data (Rashid et al., 2019; Zhao et al., 2014), we can verify our approach; indeed, the results are represented in Figs. 3 and 4 respectively. We can highlight that the indicator for the mutualistic condition is always lower than the indicator in non-mutualistic condition, with the consequence that it results more sustainable. Consequently, the mutualist behaviour allows us to obtain an improvement in the lipid production with an efficiency around of (1.53 ± 0.09) and of (1.27 ± 0.95) respectively for the two cases considered in relation to the efficiency of the single species culture. So, we can conclude that the mutualistic interactions represent an improvement the biodiesel production.

3. Results

The sustainable use of the earth limited resources represents the key for resource efficiency. Natural resources (metals, minerals, fuels, water and land, etc.) are fundamental for the economy because they represent the vital inputs for all the economic processes. The demand and use of resource materials is continuously increasing (Alonso et al., 2012). In relation to this topic it is possible to highlight at least two kinds of risks (Valero et al., 2015):

- The supply risk, which allows us to take into account the political-economic stability of the producing countries, the concentration level of production, the potential for substitution and the recycling rate;
- The environmental country risk, which allows us to take into account the risks for the countries with weak environmental performance, to protect the environment.

In this context, we have introduced an indicator useful to quantify the sustainable resources usage in relation to their economic and environmental meaning. This has been done by introducing the entropy generation in relation to the CO₂ production weighted by the useful results of the considered process. Furthermore, the entropy generation can be expressed in kWh (Lucia and Grisolia, 2018b); so, it is possible to introduce a link to a reference energetic cost, for example the cost of the electric energy, enabling the comparison among different processes in relation to the desired product obtained.

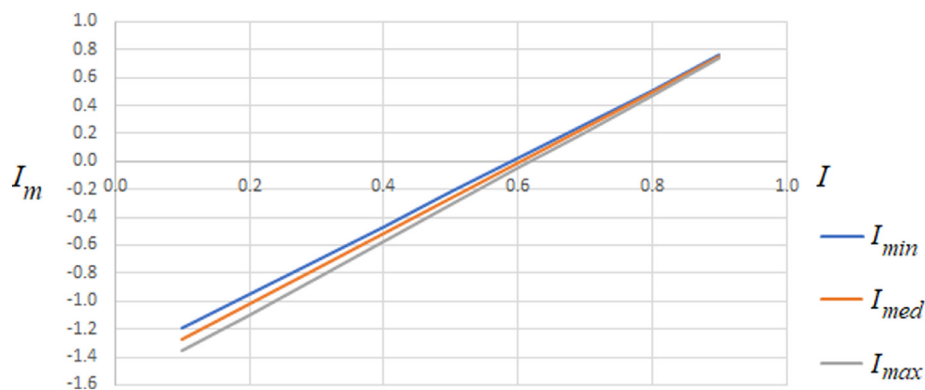


Fig. 3. Mutualistic indicator vs non-mutualistic one in relation to the better and worst condition of growth in non-mutualistic conditions, calculated by using the data collected in Ref. Rashid et al. (2019).

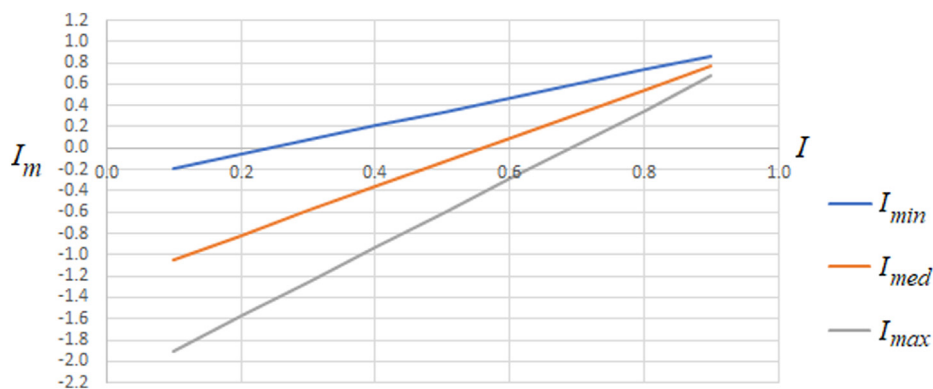


Fig. 4. Mutualistic indicator vs non-mutualistic one in relation to the better and worst condition of growth in non-mutualistic conditions, calculated by using the data collected in Ref. Zhao et al. (2014).

Moreover, the expression of our indicator allows us to evaluate the sustainability of the considered process because the entropy generated is weighted by the desired product, which means that lower is the indicator value higher is the sustainability of the process.

Lastly, the use of our indicator in the analysis of biofuel production allows us to suggest that a natural optimisation for the biofuel production process is the exploitation of a natural behaviour that can occur between two different species of interacting living organisms, or the introduction of the concept of mutualism. Indeed, mutualism allows us to improve the lipid production useful for the biodiesel production. In this context, we have introduced a simplified approach useful to evaluate the efficiency of mutualism, in order to quantify the optimisation of the process in relation to the same biochemical process carried out by the single species. The mutualistic efficiency results 1.53 times the efficiency of the lipid production of the single species.

4. Conclusions

Nowadays, the human history has come to a crossroad, driven mainly by social and economic deepening, which has led to complex dynamics and to a difficult to manage socio-economic system. As a matter of fact, both the socio-economic degradation and the environmental problems are continuously growing (Hathaway and Boff, 2009). At the same time, new opportunities for an improvement are deriving from scientific and technological advances in fields such as healthcare and to the growing of consciousness of environmental issues.

Economy as a physical system (Cleveland and Ruth, 1997; Gowdy and Mesner, 1998; Hammond and Winnett, 2009; Kerschner, 2010; Levallois, 2010) can be studied by Laws of Thermodynamics; indeed, it can be introduced by defining the system boundary in relation to producers and consumers of goods and services and the intermediate inputs and final output. Moreover, it must be considered also the environment, which represents the set of all the natural resources and the sinks, but also the place which receives the wastes of all human activities. Energy is the fundamental quantity for all the transformations and transitions within the system (Faber et al., 1990; Feidt et al., 2012). During the social and economic development humans must increase their knowledge about the technologies related to the useful processes. Lastly, due to the Second Law of Thermodynamics, high-quality energy is degraded to produce work.

Sprenge (1988) introduced the evaluation of the economic activities in relation to the importance of their output by a measure of their information and their efficiency.

Consequently, we stress that the choice among alternative technologies can be based on entropy, because entropy is the thermodynamic quantity related both to information and to efficiency (Lucia and Grisolia, 2017).

Since the '80, optimisation of energy processes and systems has been reconsidered (Curzon and Ahlborn, 1975), and Bejan introduced a new viewpoint of maximisation of power with heat engine models associated to heat transfer irreversibility, with the result that maximum power corresponds to minimum entropy generation rate (Bejan, 1994), or maximum entropy generation, which agrees with the Gouy–Stodola theorem (Lucia, 2013c,a). So, entropy generation analysis has shown to be a design tool to recognise system improvements, but also a measure of sustainability. The process with the lower entropy generation rate

is more sustainable than others because it is able to realise the energy conversion more efficiently (Kowalski et al., 2013; Hepbasli, 2008). Moreover, recently, it has also been pointed out the fundamental role of the thermodynamic analysis of fluxes and irreversibility in biology systems, economy, ecology and more in general in physics, chemistry, bioeconomy, biology and engineering, with particular interest in optimisation, design and control on systems behaviour (Rocha et al., 2018; Lucia et al., 2016; Lorente and Bejan, 2019; Lucia and Grisolia, 2019b; Reis, 2006; Gulotta et al., 2018; Lucia et al., 2017; Lorenzini et al., 2017; Lucia and Grisolia, 2018a; Clausse et al., 2012; Bejan et al., 2000; Lucia et al., 2015).

So, we have introduced a new indicator which allows us to take into account the cooperative effect of the interaction between technological, economical and social requirements of sustainability by means of thermodynamics. The result is an indicator which allows us to take into account:

- The effect of the human activities on the environment, by considering the thermodynamic waste by using the entropy generation;
- The effect on economy and society is considered in the total hour of labour, but what is very interesting is the GDP disappears, and this is a concrete answer to the recent Nobel laureate Joseph E. Stiglitz pointed out (Stiglitz et al., 2010) and responds to the European Commissions initiative “Beyond GDP” (Goossens et al., 2007).

In relation to the resource consumption, we have highlighted the fundamental role of the exergy flows, by which we can evaluate the entropy generation.

Now, we will focus our comments only on biofuels because the different applications on the plants are examples usually discussed in literature (Bejan et al., 1996). So, in relation to the lipid production for biodiesel from microorganisms, we can highlight that two mutualistic species improve the lipid production with higher efficiency. In order to evaluate this effect we have introduced a simple analytical model. Its limit is that nature is complex and non-linear, so our model represents a simplified approach to obtain quantitative results, without a deep analysis of the biophysical processes.

Indeed, biotechnology has historically utilised organisms for a variety of purposes. Recently, a directed modifications of organisms for chemical production has been developed (Jin et al., 2016). Indeed, changes in available information present in the microorganisms DNA may be useful to improve the biofuels production (Gimpel et al., 2013; Goers et al., 2014). But, the synthetic biological improvement can be considered more effective if constrained by a well defined aim, which can be pointed out by a deep analysis of the natural behaviours of the microorganisms themselves (Clay and Fong, 2013). We have developed our analysis just with this aim. We have highlighted that a natural optimisation of the lipid production consists in the co-cultivation of the microorganisms, so that a driven approach for any synthetic biological manipulation can be to improve this natural behaviour, with the result of amplifying the spontaneous behaviour of the microorganisms. Symbiosis improves some favourable aspects of the biofuel production; indeed:

- In relation to ethics, symbiosis improves the productivity of the algae and bacteria, with the consequence of a reduction of surface required for their cultivation;
- In relation to technics, symbiosis increases the optimisation of nutrients and water used with the related decreasing in the request of molecules and energy required for the cultivation of the algae and bacteria; consequently, it generates a reduction in local pollution;
- In relation to economics, symbiosis increases the profit because it increases the productivity with a decrease of the requests in energy and nutrients.

CRediT authorship contribution statement

Giulia Grisolia: Conceptualization, Methodology, Writing - Review & Editing, Visualization, Data Curation, Validation. **Debora Fino:** Conceptualization, Investigation, Funding acquisition, Resources. **Umberto Lucia:** Conceptualization, Methodology, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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